

Supporting Information

Intermolecular π - π stacking interactions made visible

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1_2_mixing_2ml.mp4	adding 2 to 1 at 2.2 mL total volume
1_2_mixing_11ml.mp4	adding 2 to 1 at 11 mL total volume
1_2_mixing_11ml_sim.mp4	mixing 2 and 1 simultaneously at 11 mL total volume
1_2_mixing_22ml.mp4	adding 2 to 1 at 22 mL total volume
1_2_mixing_55ml.mp4	adding 2 to 1 at 55 mL total volume
1_oXy_mixing_55ml.mp4	adding <i>o</i> -xylene to 1 at 55 mL total volume

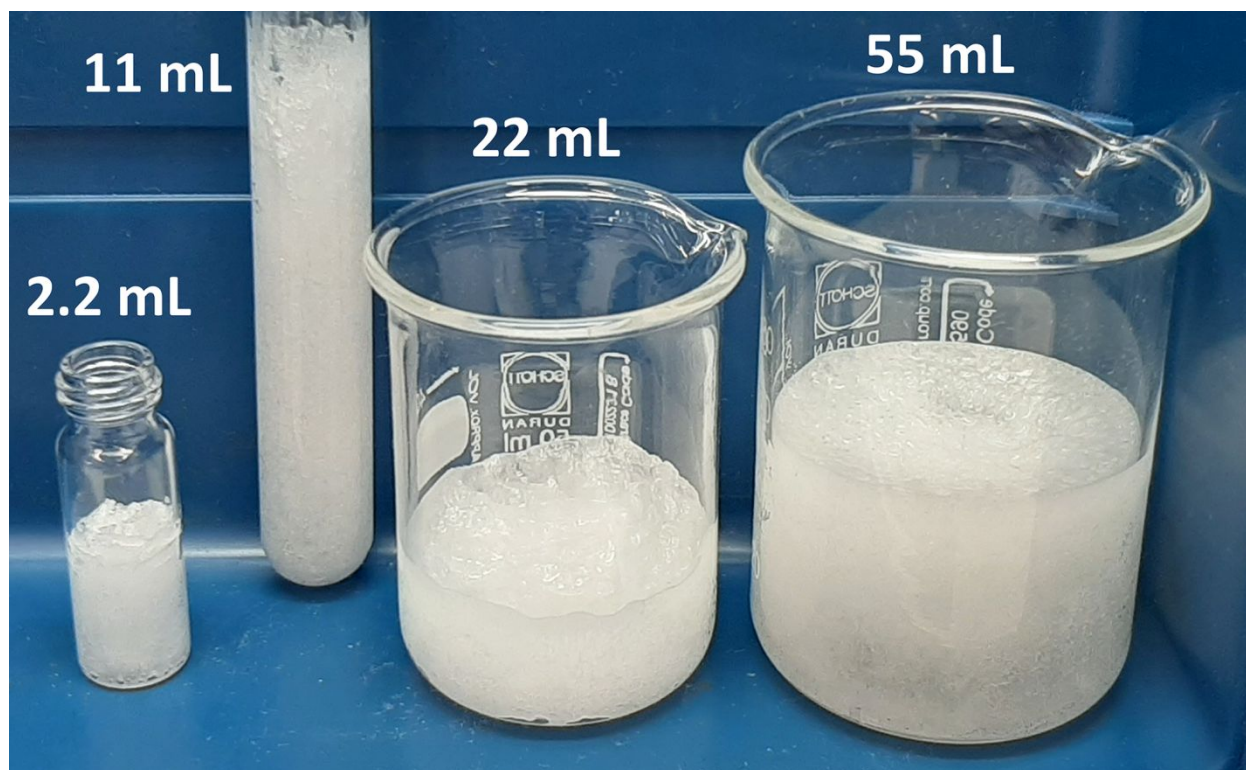


Figure S1. Results after mixing **1** and **2** at the indicated total volumes. A movie of each experiment is provided in the supplementary information as respectively 1_2_mixing_2ml.mp4, 1_2_mixing_11ml.mp4, 1_2_mixing_22ml.mp4 and 1_2_mixing_55ml.mp4.

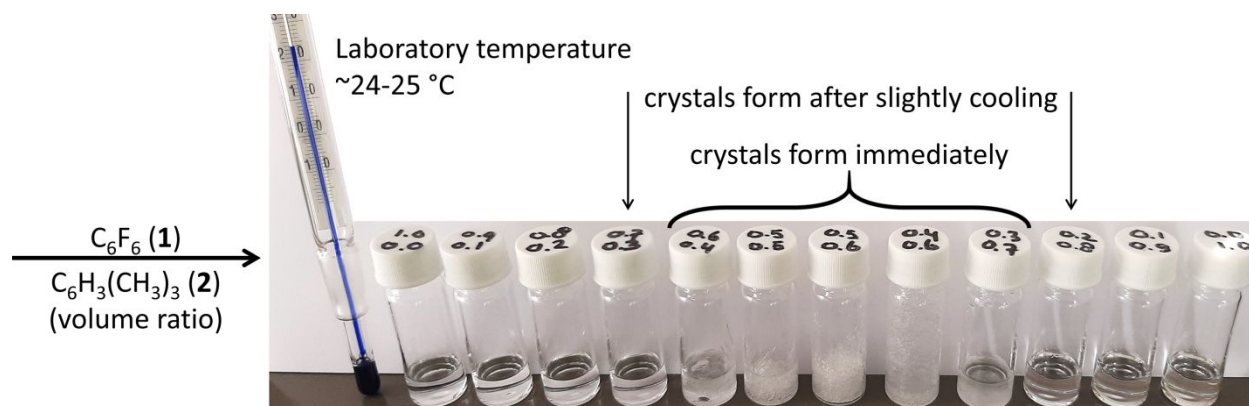


Figure S2. Vials after mixing **1** and **2** at different molar ratios (1 mL total volume) with on the far left pure **1** and on the far right pure **2**. See also Table 1.

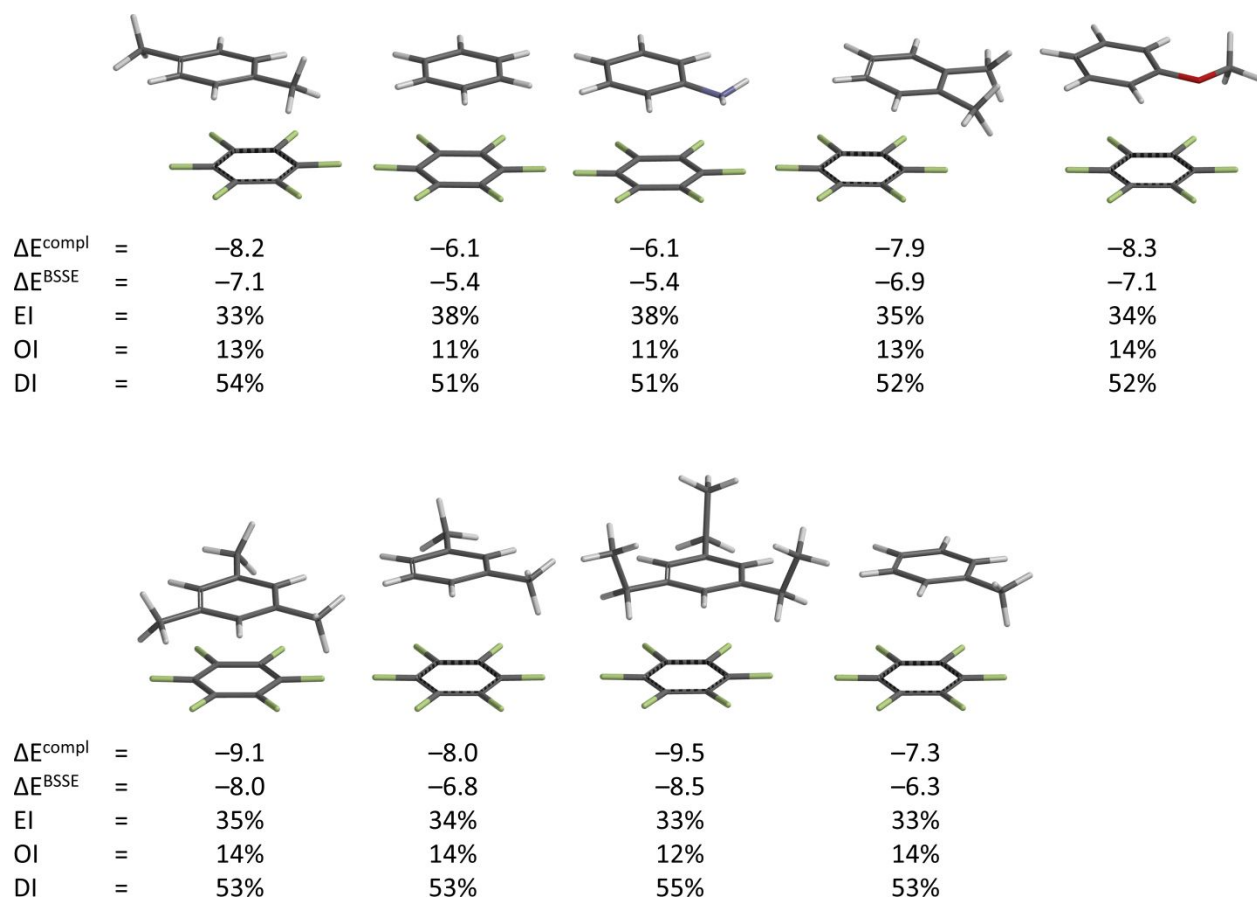


Figure S3. Perspective views of π - π stacked dimers calculated with DFT of hexafluorobenzene (**1**) with the aromatics shown in Figure 3. Also given are the complexation energy (ΔE^{compl}), the interaction energy that was corrected for the basis set superposition error (ΔE^{BSSE}), and an energy decomposition analysis divided (in % of the total attractive forces) in electrostatic interactions (EI), orbital interactions (OI) and dispersive interactions (DI). See materials and methods for details. Energies in $\text{kcal}\cdot\text{mol}^{-1}$.

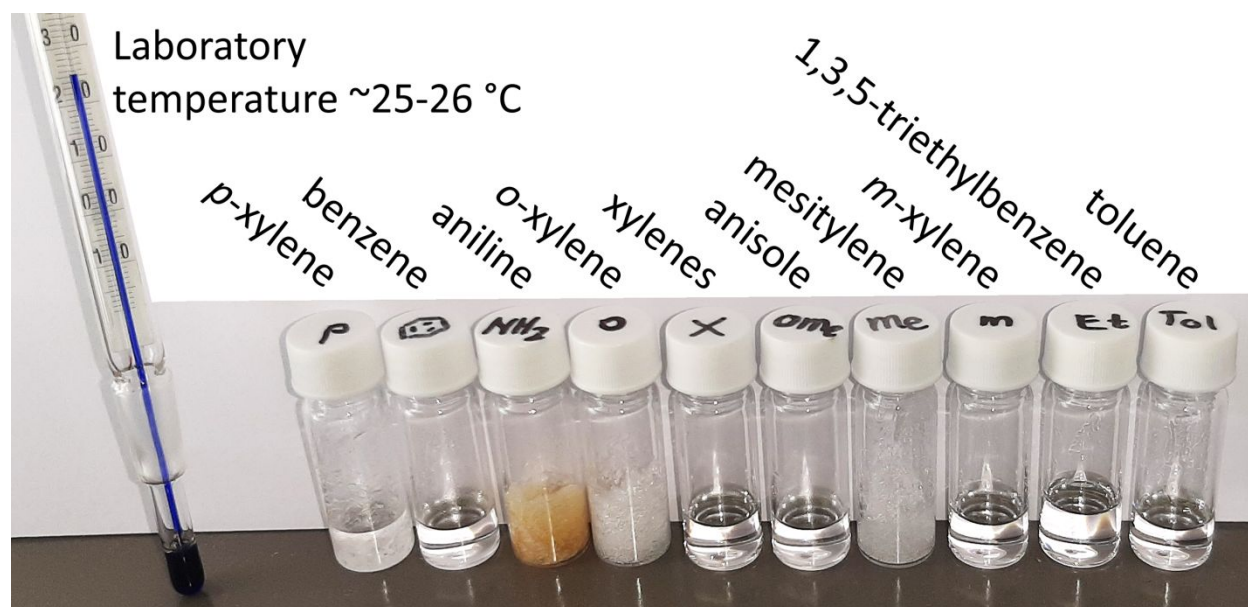


Figure S4. Vials after mixing **1** and an equimolar amount of the indicated aromatics (1 mL total volume).

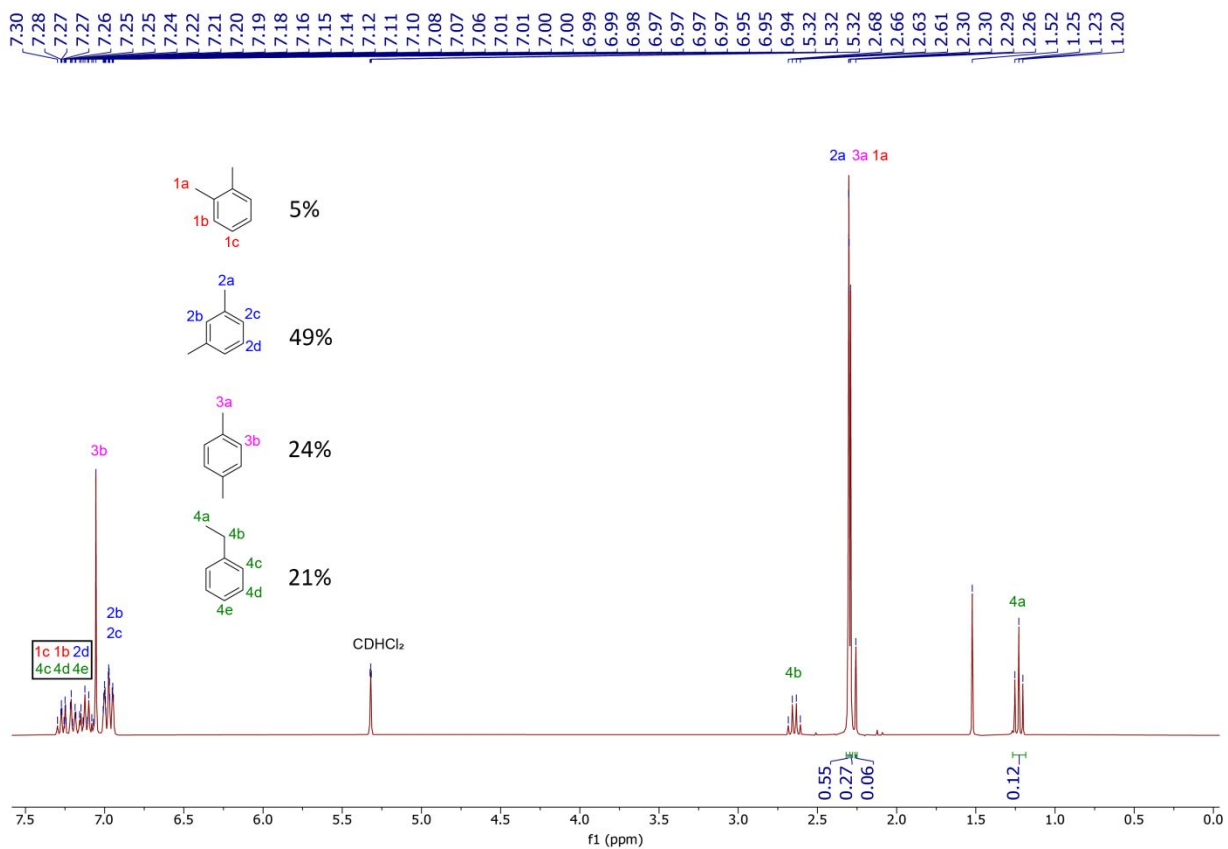


Figure S5. The component distribution of the xylenes mixtures of isomers was determined by ^1H -NMR spectroscopy using a Bruker Avance Neo NMR machine (spectrometer frequency 300.11 MHz). The compound was measured in CD_2Cl_2 and the shown chemical shifts are relative to tetramethylsilane with residual CHDCl_2 as internal standard.

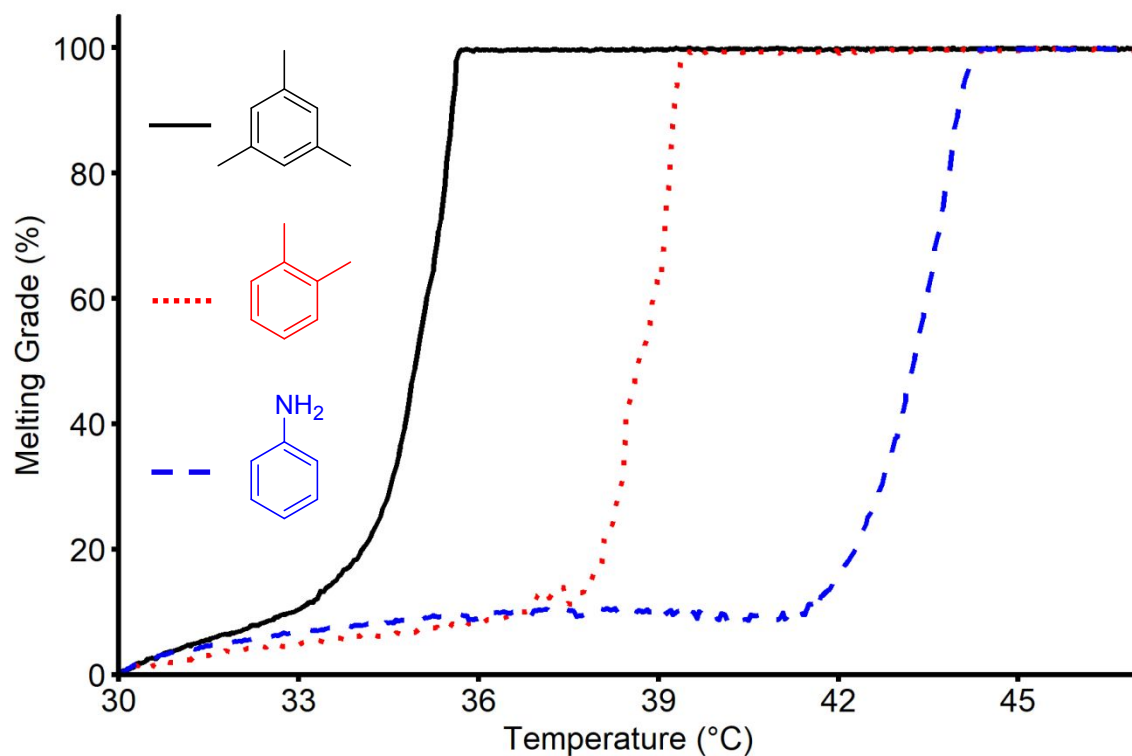


Figure S6. Melting point curves for the crystalline material obtained after mixing equimolar quantities of hexafluorobenzene (**1**) and mesitylene (**2**, black solid line), *o*-xylene (red dotted line) or aniline (blue dashed line). The curves were recorded using a Büchi M-565 automated melting point apparatus starting at the current idle temperature of the machine (27 °C) and ramping the temperature by 0.2 °C per minute until the samples were fully molten.

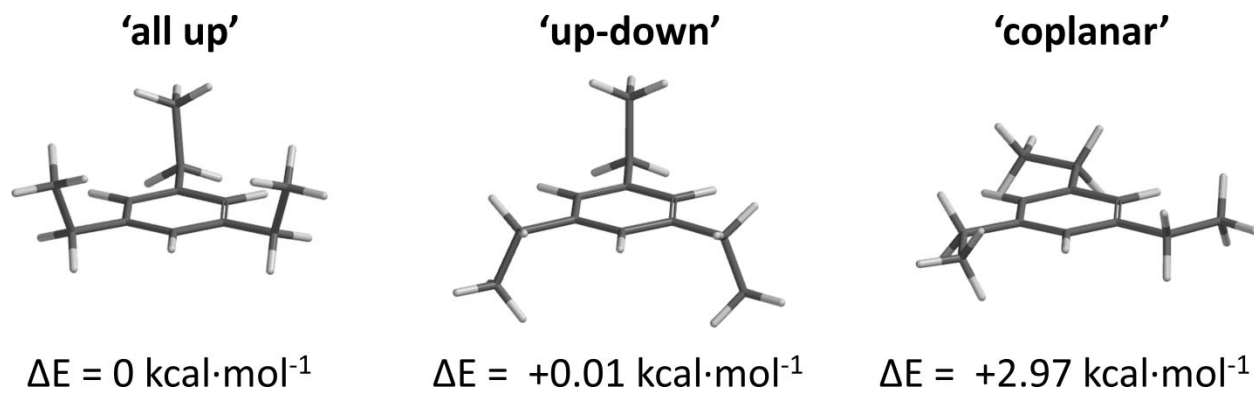


Figure S7 Table S1. Interaction energies of [1...2] computed with various methods. Three conformers of 1,3,5-triethylbenzene calculated as the DFT/B3LYP-D3/def2-TZVP level of theory with the indicated relative energies.

Table S1. Interaction energies in kcal·mol⁻¹ of [1...2] computed with various DFT methods, together with the approximate computational cost of the geometry optimization of [1...2] on one processor running at about 4 GHz (data taken from optimizations on a Ryzen Threadripper 3970X sTRX4 with 128 GB of DDR4-3200 RAM). To estimate the actual computational time these values have to be divided by the number of processing cores in the computer used. Also given are the energies using several molecular mechanics and semi-empirical methods (all took less than 5 seconds). Pople's (6-31G, 6-31G**), Dunning's (cc-pVTZ) and Ahlrichs&Weigend's (def2-TZVP) basis sets were used. The functionals selected used a (meta) generalized gradient approximation (PBE, TPSS) and the global hybrid (B3LYP, M08-HX) or range separated (ω B97X, M11) refinements thereof. The D3 dispersion correction was used with the PBE, TPSS, B3LYP and ω B97X (not available in Spartan for the M08-HX and M11 functionals). The method used in the main text (B3LYP-D3/def2-TZVP) is highlighted in bold; the methods that gave an energy deviating less than ± 0.5 kcal·mol⁻¹ from this value are highlighted in green, those deviating less than ± 1.0 kcal·mol⁻¹ are highlighted in blue.

	6-31G	6-31G**	cc-pVTZ	def2-TZVP
PBE-D3	-12.9	-12.2	-9.5	-8.6
	0.6 h	0.8 h	11 h	7.4 h
TPSS-D3	-12.8	-12.3	-9.7	-8.6
	0.8 h	4.3 h	4.3 h	9.9 h
B3LYP	-4.3	-3.8	-1.7	-1.0
	1.1 h	2.8 h	54 h	38 h
B3LYP-D3	-14.3	-13.5	-10.2	-9.2
	0.8 h	3.5 h	85 h	52 h
ω B97X-D3	-12.5	-11.4	-9.8	-9.0
	1.7 h	1.8 h	54 h	51 h
M08-HX	-13.9	-12.3	-10.2	-8.3
	4.1 h	4.6 h	141 h	70 h
M11	-13.4	-12.3	-9.7	-8.6
	3.8 h	4.3 h	11 h	9.9 h

Molecular Mechanics:

MMFF = -8.8; SYBYL = -8.5

Semi-Empirical:

AM1 = -0.5; MNDO = -0.3; PM1 = -0.9; PM3 = -0.9; PM6 = -2.3

The 6-31G and 6-31G** basis sets are the fastest, but result in an overestimation of the interaction energy, regardless of the functional used. The cc-pVTZ and def2-TZVP were slower but nearly all fall within a ± 0.5 (green) or 1.0 (blue) kcal·mol⁻¹ energy tolerance relative to the method

reported in the main text (in bold; B3LYP-D3/def2-TZVP). The B3LYP functional gave a large underestimation of the energy when the D3 dispersion correction was not applied. The uncorrected M08-HX and M11 performed reasonably well with cc-pVTZ or def2-TZVP basis sets. The interaction energies computed with molecular mechanics are surprisingly accurate. This is likely a coincidence, as it is well-known that molecular mechanics are poorly suited to obtain reliable energy data, particularly when it comes to non-covalent interactions. The semi-empirical methods all vastly underestimate the interaction energy.

For the purpose of a student project, the method to use will depend on the computing power available. Based on the data in Table S1 we recommend the TPSS-D3/cc-pVTZ level of theory. This method used about 4 hours of single-core computational time, which will be about a quarter of an hour on an octa-core computer (which are increasingly widespread). If only an approximate geometry is required, all the faster methods can be used (including molecular mechanics and semi-empirical methods).